6.—Nitrogen oxide levels in suburbs of Perth, Western Australia

by G. A. Bottomley[1] and F. C. Cattell[2]

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Abstract

Nitrogen oxide determinations are reported for two residential suburbs southwest of the central city area of Perth, Western Australia. Daily measurements for the period 10 a.m. to noon during 1971, 1972 and 1973 show that the levels of nitrogen oxides in the atmosphere are low in comparison with overseas major urban areas. The day to day values fluctuate considerably but periodogram analysis detects a seven day cycle which reflects local traffic flows with highest values on Fridays and the lowest on Sundays. The thirty day moving average shows a seasonal pattern where average values are low from about August to April and rise to a pronounced peak in May and June (late autumn). Data is given for autumn evenings when local meteorological conditions often result in shallow inversions about sunset. These inversions are coincident with peak traffic flow and concentrations of NO_x as high as 47 pphm have been detected on such evenings. Some limited monitoring of photochemical conversion of NO to NO_2 and production of ozone has been undertaken.

Introduction

The residents of Perth, Western Australia, ordinarily enjoy atmospheric quality and clarity which are remarkably good for a city with more than three-quarters of a million inhabitants. Partial explanations are adequate mixing and good ventilation (the mean wind speed is 15.6 km/hour) and the location and control of industrial and other pollutant sources. In the City and most residential suburbs the levels of smoke, sulphur dioxide and particulates are modest. However, motor vehicle use has risen sharply in the last decade and the trend continues. Because of the intense and prolonged sunshine (average 2 850 hours annually) pollution from car exhausts and photochemical effects are of public interest. We report here concentrations of oxides of nitrogen at three suburban sites recorded chiefly in 1971, 1972 and the first half of 1973.

Relevant geographical information

General

The City proper and much of the Metropolitan residential areas are on the Swan Coastal Plain at elevations less than 70 metres above sea level. Fifteen kilometres to the East the Darling Scarp rises sharply to above 300 metres. Most traffic generated by the business and residential areas is within a radius of fifteen kilometres of the City centre.

[1] Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009.

[2] Division of Cloud Physics, C.S.I.R.O., Epping, N.S.W. 2121.

Recording sites

Air samples were taken at about two metres above ground level at three locations (see Figure 1).

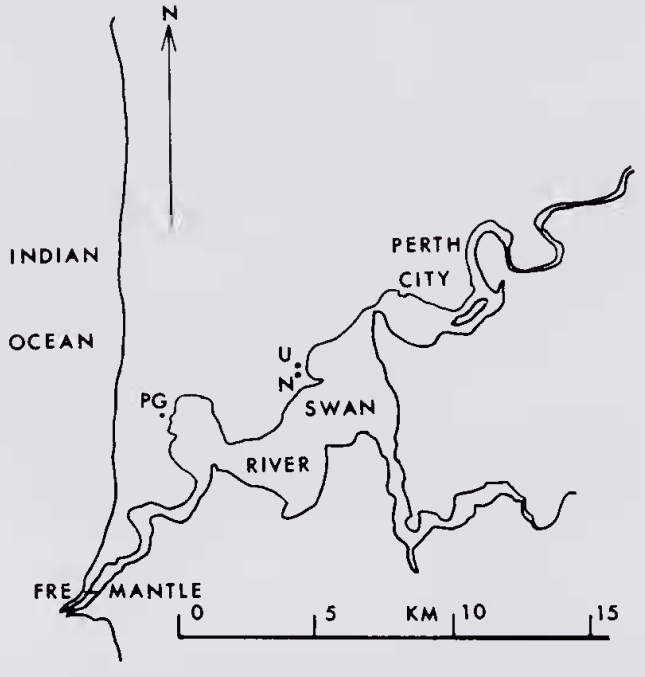

Figure 1.—Map showing University site (U), Nedlands Site (N) and Peppermint Grove Site (PG) in relation to Perth.

University site.—The University of Western Australia campus five kilometres South West of central Perth business area. Most of its forty hectare area is grassed but it includes car parks for about two thousand vehicles. To the North East is four hundred hectares of Kings Park with bush, botanic gardens and open space and to the East and South East there is a broad stretch of the Swan Estuary, hereabouts two or three kilometres wide. On the West the University is flanked by residential areas.

Nedlands site.—A private residential area about three hundred metres to the South of the University sampling site.

Peppermint Grove site.—A private residence ten kilometres South West of the city centre, within one and a half kilometres of the Indian Ocean and close to the open reaches of the lower Swan. The area includes much open space and is not near any recognisable industrial sources though domestic gas and oil appliances are in normal use for water and space heating, as at the other two sites.

Analytical procedure

Saltzman's method (Katz 1968, p. 80) with permanganate oxidation of the nitric oxide was used to determine total nitrogen oxides NO_x. Air was usually sampled at about twenty litres per hour and for two hours. The absorbing reagent, N-(1-naphthyl)ethylene-diamine dihydrochloride with sulphanilic acid in aqueous acetic acid solution was kept in very subdued light during prior storage and until the spectrophotometric determination was completed. Direct sunshine degrades the red azo compound.

The values are cited as parts per hundred million by volume pphm) of the combined oxides NO plus NO_2 unless a distinction is made in the context. The conversion factor is:

18.8 pphm = 1 microgram metre^{-3} (25°C)

Measurements at the University of Western Australia

Two hundred determinations on outside air at the University Site were taken sporadically between June 1970 and June 1971 at various times of the day and night. Table 1 summarises these exploratory results in histogram form.

Table 1

General results in preliminary survey at University Site 1970-1971

NO_x at University Site (mean value over period)	Number of Observations June 1970—June 1971
pphm	
0·0 to 0·99	27
1·0 to 1·99	63
2·0 to 2·99	39
3·0 to 3·99	11
4·0 to 4·99	16
5·0 to 5·99	9
6·0 to 6·99	6
7·0 to 7·99	4
8·0 to 8·99	1
9·0 to 9·99	3
Above 10·00 (16·4, 23·6)	2
	181

The low values are evidence for the ability of Perth air to disperse contaminants. Particularly in South Westerly air streams in winter and during the regular afternoon sea-breeze (the Fremantle doctor) in summer, values as low as 0.2 pphm have been recorded. However, there are occasional periods of calm air and poor mixing conditions which correlate with higher levels of NO_x. Table 2 sets out the highest values recorded June 1970 to June 1971 together with comments on atmospheric conditions. We consider it most unlikely that these occasional measurements would have detected the highest levels experienced that year. Newspaper reports of the highest value recorded, 23.6 pphm, 8 a.m. to 10 a.m. April 29, 1971, provoked external criticism that emissions from a small oil-fired boiler in the University grounds were responsible, a view the authors do not endorse. To eliminate this possible bias sampling was transferred to the Peppermint Grove residential site.

Table 2

Highest values in preliminary survey at University site 1970-1971

Date	Approx. Time	Value NO_x pphm.	Comment
1970			
June 18	4– 6 p.m.	5·4	
June 23	8– 9 a.m.	6·7	
	9–10 a.m.	7·1	
July 17....	9–10 a.m.	9·5	
July 24....	4– 8 p.m.	8·2	
July 25....	4– 8 p.m.	5·4	
Aug. 3	6– 8 p.m.	6·0	
Aug. 4	9–11 a.m.	9·1	Blue light-scattering material evident between University buildings.
	4– 6 p.m.	5·2	
	6– 9 p.m.	16·4	
Sept. 25	8–10 a.m.	5.9	
Sept. 29	7– 9 a.m.	7.6	
Sept. 30	7–10 a.m.	6·0	
1971			
April 1	8–10 a.m.	6.0	
April 2	4– 6 p.m.	5·2	
April 20	8–10 a.m.	6·8	Anticyclone continues for week, Herdsman Lake vegetation on fire two days previous
April 21	8–10 a.m.	7·2	
April 28	8–10 a.m.	5·8	
April 29	8–10 a.m.	23·6	City not visible from University (three miles) at 10 a.m. because of ' white-out ' Clears partially by 11.00 a.m.
	10–Noon	7·8	
April 30	8–10 a.m.	9·0	' Blue haze ' again
May 1	8–10 a.m.	6·5	
May 6	8–10 a.m.	5·8	' Grey-out '. City just visible at 10.00 a.m. from University.
May 7	8–10 a.m.	5·0	
	5– 7 p.m.	5·8	

Peppermint Grove morning series

June 1971 to July 1972

Measurements were made 10 a.m. to noon each day for more than a year and the results are set out in Table 3. The daily values fluctuate considerably with the weather circumstances and include many very low values. The maximum values 15.0 and 12.7 pphm recorded respectively on May 12 and June 8 1972, bearing in mind the greater distance of the Peppermint Grove site from the City, approach comparability with the University maximum on April 29, 1971. The monthly averages and the maximum values each month show progressive variation in levels of NO_x with a pronounced maximum in autumn and early winter months. Figure 2 shows the 'thirty day moving' average as a function of the mid-date of the averaged sequence.

Our hypothesis is that NO_x is generated by emissions from vehicular traffic in the morning rush hour and that the recorded levels reflect the inability of the air in each day to disperse that chemical burden. Information supplied by the Bureau of Meteorology for the mean monthly 7 a.m. mixing depth (1966-1969 inclusive) shows values which range from one hundred and thirty metres to two hundred and ten metres, with the lower values in May-August. The routine radiosonde ascents may

Table 3

Results of year long survey of morning values at Peppermint Grove 1971 and 1972

pphm. $NO + NO_2 = NO_X$ *10 a.m. to noon daily*

(140*a Forrest Street, Peppermint Grove*)

DAY	June 1971	July	Aug.	Sept.	Oct.	Nov.	Dec. 1971	Jan. 1972	Feb.	Mar.	Apr.	May	June	July 1972
1	....	6·9	0·5	1·6	0·8	1·2	0·4	0·6	0·2	0·6	0·6	3·4	6·3	1·6
2	....	2·5	1·5	0·9	0·9	0·6	0·3	0·6	0·2	0·5	0·6	3·3	1·0	0·7
3	....	1·7	2·1	1·0	1·1	0·6	0·2	0·6	0·2	0·5	0·6	2·6	1·9	1·1
4	....	1·0	0·8	1·1	0·8	0·9	0·2	0·6	0·7	0·5	0·4	1·7	1·0	2·2
5	....	1·5	3·9	0·8	0·8	....	0·2	0·6	0·7	0·6	1·1	1·0	2·8	4·6
6	....	3·3	1·0	1·1	0·9	....	0·2	0·6	0·7	0·7	0·7	1·1	2·0	0·8
7	1·5	4·7	3·5	1·0	0·8	....	0·3	0·5	0·6	0·7	0·7	1·5	5·0	1·7
8	1·0	2·5	1·2	1·8	0·9	....	0·4	0·5	1·0	0·7	0·9	3·3	12·7	0·8
9	1·5	1·7	1·4	1·1	0·8	....	0·6	0·4	0·8	1·3	0·2	5·0	11·0	0·9
10	0·9	7·3	1·3	0·9	0·6	....	0·5	0·5	0·7	0·8	0·8	1·3	2·6	1·1
11	3·8	4·0	1·5	1·1	1·0	0·7	0·5	0·6	0·7	0·8	0·9	2·0	1·3	2·0
12	2·7	1·3	0·9	1·1	1·0	0·6	0·7	0·5	0·8	0·2	1·3	15·0	0·8	1·4
13	1·5	2·2	0·8	1·1	0·8	0·6	0·5	0·5	0·9	0·2	2·0	1·0	0·4	0·9
14	1·1	1·7	1·7	2·0	0·9	0·7	0·7	0·4	1·3	0·2	0·9	0·8	0·4	0·9
15	1·6	2·2	0·6	1·7	1·0	0·4	1·0	0·6	0·8	0·2	2·3	1·1	0·7	4·5
16	1·1	2·3	0·8	1·9	1·0	0·4	1·1	0·7	0·9	0·5	1·8	3·5	0·4	2·1
17	3·8	2·2	0·8	1·4	0·6	0·5	0·7	0·7	0·6	0·3	1·4	4·0	0·5	3·0
18	7·2	2·1	1·6	1·4	0·8	0·4	1·0	0·7	0·8	0·3	1·0	1·9	2·0	1·7
19	1·6	2·2	2·0	1·0	1·0	0·4	0·9	0·7	1·1	0·2	0·9	1·8	2·0	5·2
20	1·2	0·9	1·8	1·1	0·7	0·5	1·0	0·9	1·1	0·3	1·0	1·2	2·0	4·5
21	6·5	0·6	....	0·9	0·9	0·9	0·9	0·9	....	0·7	2·5	2·0	2·3	3·0
22	2·5	0·8	....	0·7	0·7	0·5	1·1	0·8	1·5	0·4	1·7	1·7	0·8	2·0
23	6·8	1·0	....	0·8	0·9	0·5	0·8	1·2	1·3	0·6	1·0	1·9	2·5	1·6
24	3·8	1·4	....	0·8	0·8	0·6	1·1	0·6	1·1	0·4	1·8	2·0	1·8	0·4
25	6·5	2·0	....	1·3	0·9	0·6	0·8	0·6	1·0	0·5	1·1	1·7	1·0	0·4
26	6·8	2·2	....	....	0·8	0·8	0·8	0·6	0·9	0·3	1·3	1·1	0·8	....
27	4·8	1·9	1·1	1·1	1·0	1·1	0·5	0·9	0·8	0·4	4·8	0·9	1·2	....
28	6·8	1·4	0·7	0·9	0·9	0·5	0·4	0·7	0·5	0·6	7·5	1·7	0·8	....
29	2·1	1·0	0·5	1·1	0·9	0·6	0·4	0·4	0·6	0·5	3·4	1·0	4·0	....
30	2·7	1·1	0·9	0·8	0·9	0·4	0·6	0·2	....	0·5	1·6	2·0	10·3	....
31	....	1·1	0·6	....	1·0	....	0·6	0·2	....	0·5	....	0·8	....	....
Av.	3·33	2·22	1·34	1·14	0·87	0·62	0·66	0·61	0·81	0·51	1·56	2·36	2·74	1·96
Max.	7·2	7·3	3·9	2·0	1·1	1·2	1·1	1·2	1·5	1·3	7·5	15·0	12·7	5·2
Min.	0·9	0·6	0·5	0·7	0·6	0·4	0·2	0·2	0·2	0·2	0·2	0·8	0·4	0·4

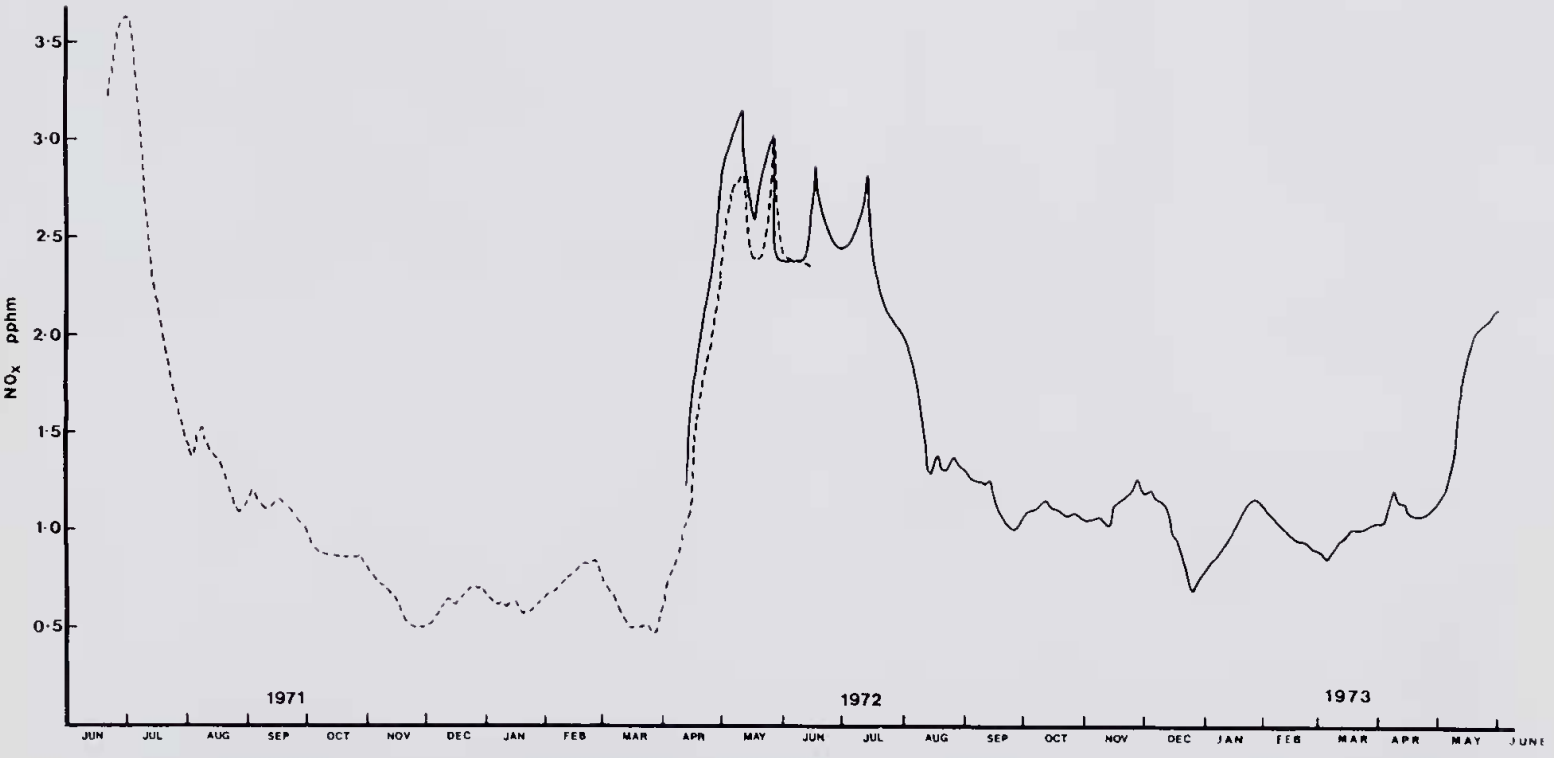

Figure 2.—Morning values of NO_x recorded at Peppermint Grove (dotted line) and at Nedlands (full line) expressed as a thirty day moving average.

not give particularly useful information about the lapse rate below the first hundred metres which is presumably the critical zone for dispersion of traffic exhausts.

Taken in the broad sense the dispersion of the air is rather generally governed by the energy flux from the sun which is very high here in summer. In the winter months the sun is at a relatively low angle and operates for less time before the start of the sampling period. The monthly averages appear to be governed substantially by this main driving force. Daily features of the synoptic weather pattern such as rain storm progressions and anticyclones are obscured by the thirty day averaging procedure but special features will be taken up later.

In general high nitrogen oxide levels correspond to days of reduced visibility, with suggestions of association with a special blue light-scattering quality. This does not require that the source of the nitrogen oxides is also responsible for the impaired visibility but indicates that at these times weather conditions are unfavourable for the dispersion of all pollutants. On days of poor visibilty any photochemical destruction of the nitrogen dioxide would be slower.

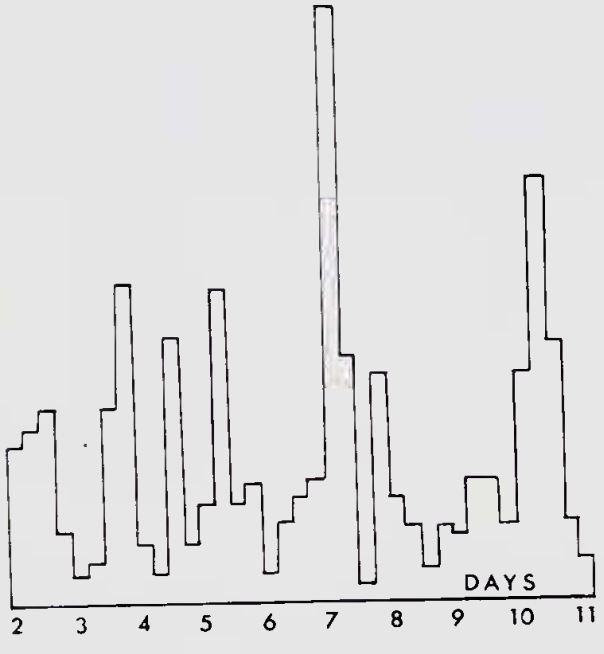

Figure 3.—Periodogram showing response against duration of cycle for the data given in Table 3.

The entries in Table 3 contain latent information which supports the car emission origin. It would be reasonable to suppose traffic flow to be substantially less on Sunday mornings in comparison with mid-week mornings. Emission release may therefore be cyclic, of period seven days, and of minimal amplitude on Sundays. The values in Table 3 were subjected by Schuster's method (Whittaker 1944) to a computer-assisted search for periodicities in the range two to thirty-two days in intervals 1/4 days. Part of the periodogram is shown in Figure 3. There is considerable evidence for a seven day component. For seven day periodicity the data can be succinctly expressed as the sum of the values recorded each Monday, each Tuesday, etc., through the week. The totals for fifty-five weeks are:

Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
70·6	67·3	72·7	90·2	98·3	75·2	58·6

a pattern which qualitatively reflects the traffic behaviour in the Metropolitan area.

Periodograms for the period March 1, 1972 to June 30, 1972 have also been run on data for twenty-four hours smoke values and sulphur dioxide values in the City. The patterns are not similar to that for the NO_x data so it is reasonable to conclude that the sources and dispersion characteristics of NO_x, SO_2 and smoke are dissimilar. In particular the seven day frequency component for the SO_2 measurements shows a mid-week rather than a Friday maximum.

Nedlands series

Mornings April 1972 to December 1972

Table 4 shows in summary form measurements 10 a.m. to noon at the Nedlands site from March 28, 1972 to June 14, 1973. Figure 2 summarises the trend of these measurements in the form of "thirty day moving averages" and displays the two series together. An interesting point is that the thirty day averages for the two sites five kilometres apart for the few weeks when simultaneous measurements were underway are similar in magnitude and in form.

A maximum mean concentration of 3 pphm in late autumn and early winter falls from the middle of July to about 1 pphm in September at both sites. In 1971 at Peppermint Grove there was a further decrease to an average

Table 4

Results of year-long-survey of morning values at Nedlands

pphm. NO_X 10 *a.m. to noon daily*

1972	Mar.*	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Average	1·51	1·70	2·67	2·95	2·23	1·38	1·18	1·15	1·11	0·97
Maximum	1·33	8·9	19·1	13·2	6·4	3·6	3·2	2·1	4·0	1·9
Minimum	0·7	0·4	0·4	0·7	0·6	0·7	0·4	0·7	0·7	0·5

1973	Jan.	Feb.	Mar.	Apr.	May	June*
Average	0·96	0·99	0·98	1·08	1·88	1·76
Maximum	2·2	1·5	1·5	2·6	5·3	3·1
Minimum	0·2	0·4	0·6	0·3	0·7	1·0

* Incomplete month.

concentration of about 0.7 pphm from November to March but at Nedlands in 1972 the average remained constant at 1 pphm. The relative contributions of the different sites and the different years to this difference cannot be estimated.

Periodogram analysis shows a similar frequency pattern to that of the Peppermint Grove data and again the totals over sixty three weeks for the weekdays are indicative of traffic origin:

Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
86·5	85·3	98·6	110·2	122·3	92·1	70·9

Figure 4 shows the daily inter-site comparisons of the 10 a.m. to noon values for a sample period in April and May 1972. The very close comparison between the rise and fall of the values above 2 pphm supports the view that both the long term average and the major observed effects are very probably typical of substantial parts of the Metropolitan area.

The correlation between the measurements at both sites for all days of the month can be estimated from the Spearman's rank correlation coefficient (Fisher 1958). If the days of the month are ranked according to nitrogen oxide values:

$$r = 1.0 - \frac{6\ \Sigma d^2}{n^3 - n}$$

where Σd^2 is the sum of the squares of the rank differences between the two sites and n is the number of days of the month. For April 1972, $r = 0.577$ and for May, $r = 0.879$, suggesting significant positive correlation. The probability, P, that such a correlation could arise by random sampling from uncorrelated data can be estimated from Student's t test where

$$t = r\left(\frac{n - 2}{1 - r^2}\right)^{\frac{1}{2}}$$

which gives for April $t = 3.7$ and for May $t = 9.9$. For each month P is less than one in a thousand for a random occurrence. Again we conclude that the same controlling factors for nitrogen oxide concentrations seem to be operative at both sites, local uncorrelated sources can play only a minor part.

Results from measurements outside the 10 a.m. to noon period

The main sequence of measurements was deliberately taken so as to avoid the traffic peak emissions but some effort has also been made to measure the effects of these.

The principal meteorological factor leading to high concentrations of car emissions is the presence of a very shallow mixing layer in the air of the Metropolitan area. Particularly on late autumn afternoons with little or no wind, as sunset approaches inversion conditions set in as the layer of air close to the ground cools by radiation to temperatures substantially below that of air at a few tens or hundreds of metres. The onset of these conditions is often apparent to casual observers in that light smoke from domestic or garden fires is retained at shallow depth with otherwise very clear air above it. The same does *not* apply to emission from tall chimney stacks where the plumes carry well above this stagnation layer.

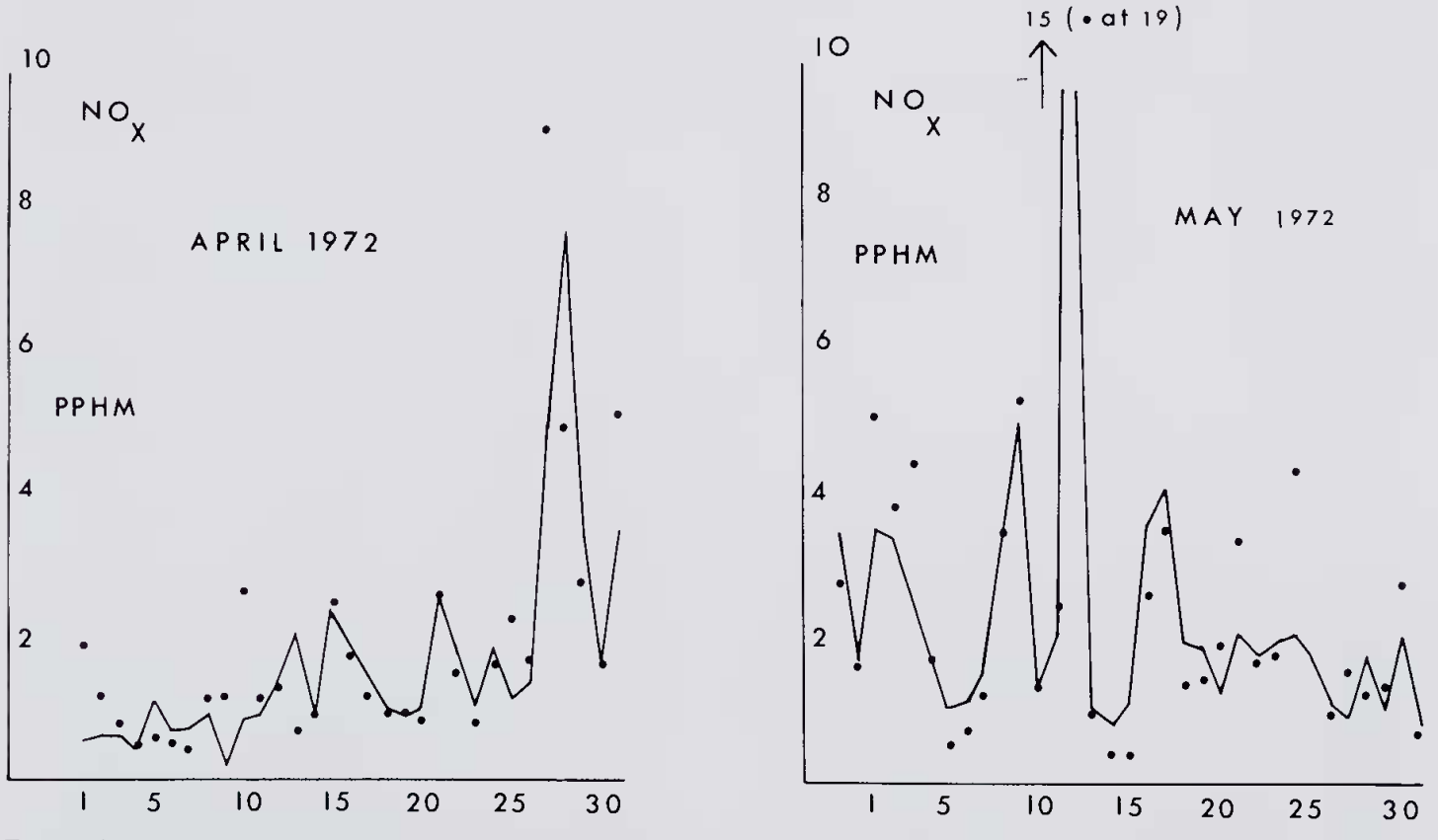

Figure 4.—Intercomparison of simultaneous morning values at Peppermint Grove (full lines) and at Nedlands (dots).

Measurements of NO_x levels were often purposefully taken during such actual or suspected (they are not visually detectable after dark) conditions. Observations outside the regular 10 a.m. to noon period were deliberately biased to times and days of anticipated higher levels and they do not represent an average overview of the early morning or evening conditions.

Table 5 lists pertinent but extreme data collected at the Nedlands site. Values taken at the same time in Peppermint Grove are broadly similar though the peaks tend to be somewhat lower and later consistent with a Westerly movement of contaminated air from the City centre across Nedlands to the coast at two to three kilometres per hour.

Table 5

Notably high measurements recorded in Nedlands 1972

Saturday, 15th April		
Above 20 pphm	1900 to midnight	5 hours
Above 25 pphm	2000 to midnight	4 hours
Peak 27·8 pphm.		
Sunday, 16th April		
Above 20 pphm.....	2100 to midnight	3 hours
Peak 23·8 pphm.		
Friday, 28th April		
Above 20 pphm.....	1900 to 2100	2 hours
Peak 32·5 pphm.		
Saturday, 29th April		
At 19·5 pphm.	300 to 500	2 hours
Wednesday, 3rd May		
Above 20 pphm.....	1800 to 2200	4 hours
Above 30 pphm.....	1900 to 2200	3 hours
Above 40 pphm.....	1900 to 2100	2 hours
Peak 47 pphm.		
Friday, 12th May		
Above 20 pphm.....	900 to 1100	2 hours
Peak 30·4 pphm.		
Tuesday, 23rd May		
Above 20 pphm.....	1813 to 2000	2 hours
Peak 30·7 pphm.		
Thursday, 25th May		
Above 18 pphm.....	1200 to 2210	10 hours
Peak 31 pphm.	(Data possibly of lower confidence limits)	
Thursday, 1st June		
Above 30 pphm.	1800 to 0100	7 hours
Peak 37·3 pphm.		
Thursday, 29th June		
Above 20 pphm.....	1900 to 2300	4 hours
Peak 29·4 pphm.		

The 1972 mid April anticyclone and subsequent stagnation spells

Thursday, April 13th, 1972 brought a distinct layer of smoke over the Metropolitan area, with the Bureau of Meteorology issuing an air dispersion alert. Friday, April 14th, was similar with smoke haze extending many kilometres out to sea and persisting well into the afternoon: a dispersion alert was issued for Friday evening to Saturday noon. The smoke is said to have originated in burning-off operations on South West farms. This agricultural burning is common at certain times in Western Australia. Similar controlled burning of forest land occurs at selected times; a major discussion of such bush-fire smoke is available (Vines 1971). Saturday and Sunday were much better optically. By midday Monday winds were affecting the City, clouds were gathering and after a calm period in the evening, wind sprang up again and rain fell early on Tuesday morning. The University wind records showed a forty hour calm starting 6 p.m. on Friday 14th. Alerted by some unexpectedly high values at Nedlands we obtained a considerable number of one hour and two hour duration measurements on April 15th, 16th and 17th. These are shown in Figure 5: similar information at other times in May and June 1972 appear in Table 5.

The extreme peak of 47 pphm on Wednesday, May 3rd, 1972 followed the formation at sunset of a very shallow stagnation layer containing smoke from domestic fires under almost calm conditions. The plume from a ship leaving Fremantle Harbour persisted virtually intact for twenty minutes.

Visual evidence that Perth's atmosphere can at times be incapable of dealing quickly with atmospheric contamination is given in Figure 6 which shows a view looking South from the University at 9.45 a.m. and 9.55 a.m on June 7th, 1972. Smoke from a fire at a distance of about eight kilometres has risen to about two hundred metres and has spread horizontally over a distance of about five kilometres. Dispersion occurred quite suddenly two hours later.

Several of the evening events were preceded by an abnormally hot day for the time of the year, but such a feature is not essential. Thursday, June 29th was a day with a maximum temperature of 13.4°C, several degrees *below* average, but again there was a radiation inversion early in the evening to give exceptionally low ground temperature. Friday, May 12th produced quite high values in the morning, yet was associated with morning mist and light fog in Kings Park and slight rain clearing from the South West around 1 p.m.

It may be informative to make extremely simplified estimates of the amount of nitrogen oxide released. Assume a cylinder of contaminated air five kilometres radius, one hundred metres deep and of average concentration 20 pphm. This contains a volume of 75×10^8 metre^3 or $3\,000 \times 10^8$ moles of gas at one atmosphere pressure. At 20 pphm it will contain 60 000 moles of NO_2, which is some 3 000 kg. The amount of NO_x involved can also be approached from emission estimates. The "Freeway" Brochure produced by the Commissioner of Main Roads (1967) shows that Metropolitan Region traffic in an earlier survey amounted to 50 000 trips per hour over a five hour weekday period 3 p.m. to 8 p.m. This is 250 000 trips with an average of say four miles per trip each evening traffic rush period. Taking the Californian 1971 standard of 4 grams NO per mile gives 6 000 kg. NO_x. To the car emission after revision for annual growth we should add of course any NO_x from fuel oil and gas consumption but only that released at very low level. It then appears that the levels observed are achievable by car exhaust emissions within the

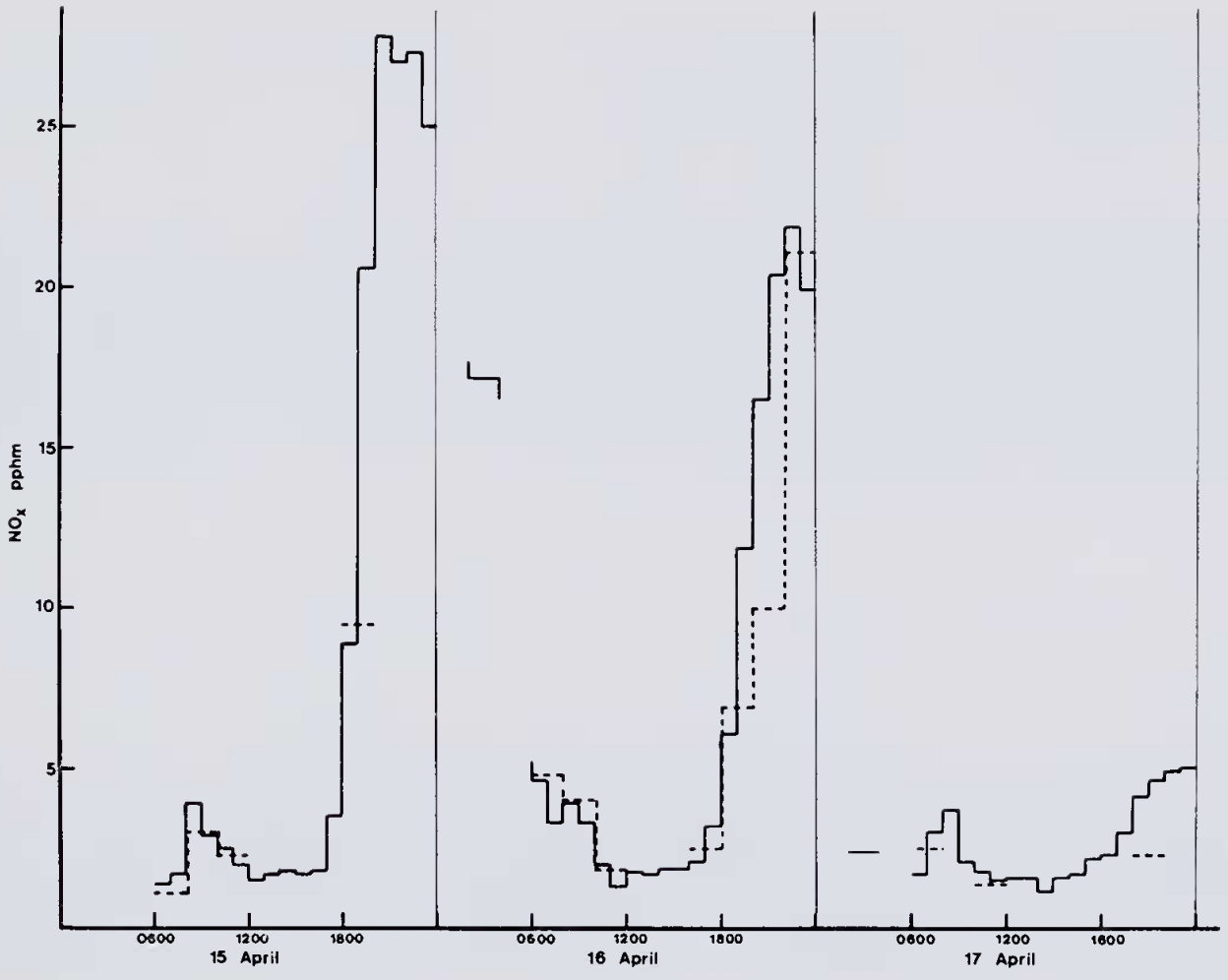

Figure 5.—Intercomparison of simultaneous values at various times for the special circumstances in mid April 1972. Full line Nedlands site, dotted line Peppermint Grove site.

Metropolitan area without invoking other sources such as bush fires which do not from other evidence (Vines 1971) appear to contribute NO_x though they may well produce smoke levels in Perth.

NO_x levels as indicators of photochemical and other pollutants

The NO_x values found as maxima in Nedlands compare at the one hour and eight hour level with those recorded as maxima for New Orleans (Zimmer 1965). This is disconcerting as it is most unlikely that the values measured at the particular sites correspond to absolute maxima in the Metropolitan area. The values justify commentary and further experimentation on other forms of car pollutants; carbon monoxide, photochemical oxidant and lead levels.

The national primary and secondary ambient air quality standards (Federal Register 1971) for nitrogen dioxide prescribed by the Environmental Protection Agency of the United States of America is 5 pphm annual arithmetic average. Our measurements even for the total oxides of nitrogen do not approach this figure and nitric oxide, for which there is no standard, predominates over nitrogen dioxide (See Figure 7) at least in the evening air for which the concentrations are greatest.

Although the nitrogen oxide concentrations are not in themselves of serious concern it is possible from them to make inferences of the simultaneous concentrations of carbon monoxide. Overseas data for automotive emissions (Hurn 1968) and experimental observations from the Continuous Air Monitoring Programs (Zimmer 1965) suggest that the carbon monoxide concentration is typically about forty times the total nitrogen oxide level. If this is true also for Perth, as seems likely, then on four of the seven nights for which concentrations of oxides of nitrogen greater than 20 pphm were measured, the U.S.A. national primary and secondary carbon monoxide air quality standards (Federal Register 1971), 9 pphm maximum eight hour concentration not to be exceeded more than once a year, were violated in some suburbs West of the central Perth area.

The levels of 20 pphm NO_x recorded several times are certainly sufficient to induce photochemical smog given sufficient hydrocarbons, except that the observed incidents occurred in the late evening. Should such levels persist into two or three hours of sunshine we must anticipate photochemical effects with the characteristic lachrymatory effects and with visibility loss. The 8 a.m. to 10 a.m. April 29th, 1971 event was possibly just such a persistent wave.

Less nitrogen dioxide than nitric oxide is emitted from combustion processes. In the absence of other contaminants the conversion of nitric oxide (at pphm concentrations) to

Figure 6.—Smoke from fire South of Swan River on June 7th, 1972. Upper photo 9.45 a.m., lower photo 9.55 a.m. Nedlands site in foreground.

nitrogen dioxide is exceedingly slow. However, in the presence of hydrocarbon pollutants and sunlight the conversion is accelerated and typically takes one to two hours. In cities where photochemical smogs occur the nitric oxide peak, formed as a result of the morning traffic, decays and is replaced by a nitrogen dioxide peak. Nitrogen dioxide absorbs light and is removed with the formation of photochemical oxidant (mainly ozone) which has a maximum concentration about noon. This sequence although typical of photochemical smog formation is modified by weather conditions.

Photochemical oxidant concentrations were measured sporadically in 1972 by the neutral buffered potassium iodide method (Katz 1968, p 86). Measurements in Nedlands showed that nitric oxide, nitrogen dioxide and photochemical oxidant concentrations behaved similarly with time to atmospheres in which photochemical smog formation occurs (Tebbens 1968) except that pollutant concentrations are much smaller. For example, as shown in Figure 7, on the 7th June 1972 a morning nitric oxide peak of 5 pphm occurred between 8 a.m. and 9 a.m. a nitrogen dioxide peak of 2.5 pphm occurred between 11 a.m. and noon and an oxidant peak between noon and 1 p.m.. This suggested that photochemical activity was occurring and is consistent with occasional subjective observations by experienced workers of a faint "Los Angeles" smell.

Oxidant concentrations were measured routinely on weekdays from October 1972 until the end of December 1972. In October, November and December maximum oxidant concentrations often occurred between 10 a.m. and 11 a.m. in the morning after which time they decreased rapidly and often remained relatively constant throughout the afternoon. The decrease which may be associated with the break up of an inversion or with the appearance of a sea breeze supports the belief that the oxidant is formed at low altitudes.

This pattern was not always followed and on 22nd November, 11th December and 16th December 1972, concentrations of greater than 6 pphm, which is the unofficial WHO goal (Bilger 1972), were measured. On the 11th December, as shown in Figure 8 an average oxidant concentration of greater than 8 pphm persisted for about two and a half hours between 1 p.m. and 3.30 p.m. This concentration is greater than that recommended by the U.S. primary and secondary air quality standards for photochemical oxidants and which is usually taken as the first indication of a mild photochemical

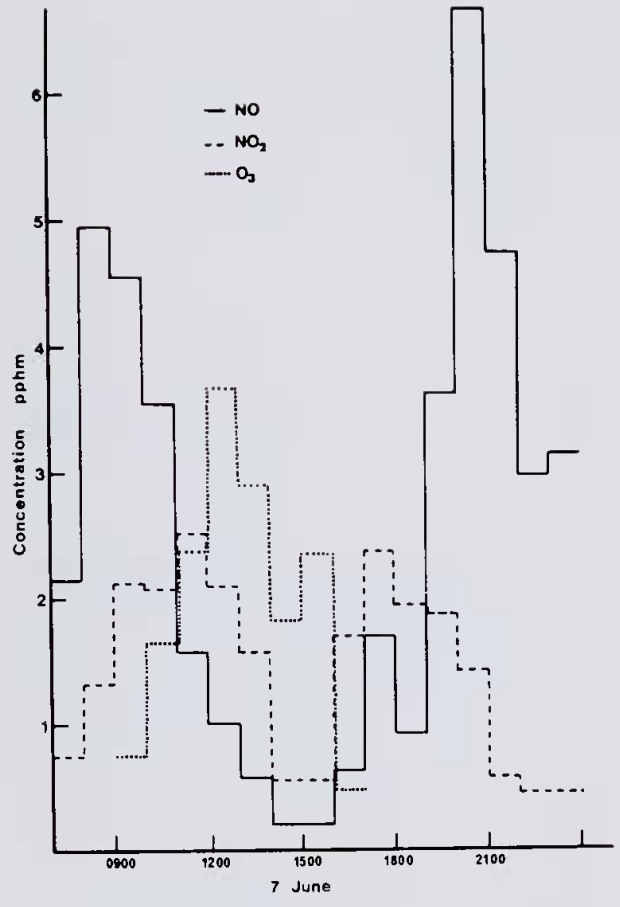

Figure 7.—Time dependence of ozone, nitric oxide and nitrogen dioxide on June 7, 1972.

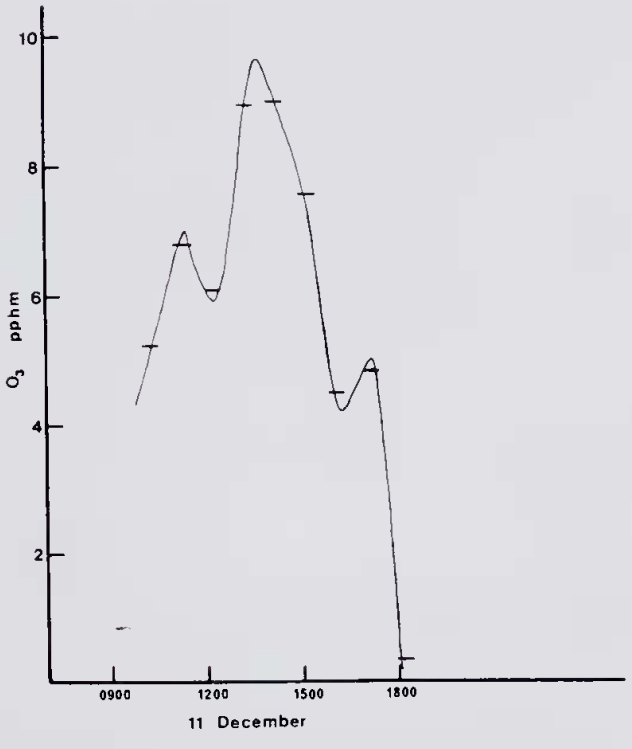

Figure 8.—Dependence of oxidant concentration on hour of day, 11 December 1972.

smog. This is the first unequivocal evidence for photochemical smog formation in Perth.

During 1973 a chemiluminescent detector, based on the reaction of ozone with ethylene was constructed. This detector follows most of the recommendations of the United States Environmental Protection Agency (Federal Register 1971), is specific to ozone and has a very fast response. Parallel measurements on a few days with the neutral potassium iodide method and with the chemiluminescent detector suggest that our earlier measurements may have underestimated the concentration of the photochemical oxidant by as much as 20%.

Studies were made of the variation with time of the ozone concentration (measured by chemiluminescence) outside the Chemistry Department. On 28th August, 1973, for example, the ozone concentration rose from 2.2 pphm at 9 a.m. to a maximum of 6 pphm at noon, remained relatively constant to 3 p.m. and decreased to 4 pphm at 5 p.m.

Occasional relatively high oxidant concentrations were measured on days on which bush fires were burning. However, insufficient measurements were made to test whether any positive correlation exists. It is possible that natural organic vapours may participate in the photochemical reaction leading to oxidant formation in which case the abnormal release of large amounts of these in bush fires could be important.

Topographic factors

Since the highest NO_x concentrations always seem associated with a shallow stagnant air layer which has accumulated pollution from vehicles and above which is clean air, the observed concentrations will depend very sharply on the precise location of the observing station. Accordingly, altitude changes of ten, twenty or fifty metres above ground levels or in buildings may be very significant especially when emissions occur over concave land surfaces. Tests should be instituted at such sites as: the Perth foreshore between the Narrows and the Causeway, Dog Swamp—a classical 'frost hollow' traversed by Charles Street, the vicinity of Cottesloe railway-station in a valley traversed by Stirling Highway (the fringe of this valley is the location of the Peppermint Grove Sampling site), and at Lake Monger, Perry Lakes, and Herdsman Lake. Sampling sites representative of the whole Metropolitan area may be difficult to select.

It was completely beyond our resources to undertake multisite routine measurements, but a preliminary investigation was mounted as follows.

About forty members of the University of Western Australia Clerical and Technical Staff Association co-operated in collecting simultaneous "grab samples" of air at different sites in the Metropolitan area. These grab samples were analysed subsequently. Because of the difficulty in converting nitric oxide to nitrogen dioxide these measurements are not completely quantitative and probably relate to the nitrogen diox-

ide component alone. However, they do provide a relative measurement and have shown that at any one time there is a wide variation in concentrations throughout the Metropolitan area. In general low values were found on the outskirts and highest values along a NW to SE corridor through the city. Some localities (e.g. Dog Swamp) consistently recorded high values and in general the ranking of sites in terms of NO_x concentrations did not vary much from day to day.

For instance, when twenty-four suburban sites were ranked accordingly to nitrogen oxides concentration at 8 a.m. on 27th April and also at 8 a.m. on 4th May, 1972 the rank correlation coefficient was 0.739 corresponding to a value of $t = 5.1$ and indicating a value for P of less than 0.1%. The correlation is apparently not as good when the concentrations of nitrogen oxides are lower. The correlation between twenty sites at 8 a.m. on 20th April and 27th April 1972 was described by a value of the rank correlation coefficient r of 0.424, a value of t of 2.0 suggesting a value of P of about 6%.

Strong correlation between sites often existed even when the measurements were made at different times of the day. For twenty-one suburban sites the rank correlation coefficient between measurements at 8 a.m. on 27th April and 9 p.m. on 17th April, 1972 was characterised by a value of $r = 0.477$, corresponding to $t = 2.4$ and $P = 4\%$.

The management of Strathern Apartments, Kings Park Avenue, kindly allowed 'grab samples' to be taken at ground floor, 14th floor and 23rd floor levels in an attempt to obtain information about vertical distribution of NO_x. No successful measurements were made even on days with well defined shallow stagnation layers. These inquiries should be prosecuted in future with fully automated equipment operating simultaneously at the three levels.

General Comment

To some extent 1972 was an exceptional year in terms of broad meteorological parameters, but 1973 was not an average year either. Whether the surprisingly high levels of NO_x measured on several days in 1972 were quite abnormal, perhaps the highest ever experienced, is a question which can only be answered by chemical measurements taken over the next several decades. In the absence of extremely detailed meteorological information about the surface inversions which have occurred in the past history of Perth it would appear unwise to assume that 1972 was a wholly abnormal year with respect to chemical concentrations.

The special position of 1972 is perhaps sufficently emphasised by the fact that ten air dispersion alerts were issued in 1972 by the Bureau of Meteorology, compared to two in the whole of 1973 and one only in the first nine months of 1974. Irre pective of future events, we contend that the analytical figures obtained in 1972 have merit in drawing attention to the special pollution features of shallow inversions and in providing a datum against which to measure any future year, typical or atypical.

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References

Bilger, R. R. (1972).—Motor vehicle emission controls for Australia. *Clean Air* 6: 44.

Federal Register (1971).—36 (84): 8187.

Fisher, R. A. (1958).—*"Statistical Methods for Research Workers"*. 13th Ed. Hafner Publishing Co., New York.

Hurn, R. W. (1968).—Mobile combustion sources. In *"Air Pollution"*. A. C. Stern ed., Vol. 3, p. 62. Academic Press, New York.

Katz, M. (1968).—Inorganic gaseous pollutants. In *"Air Pollution"*. A. C. Stern ed., Vol. 2, p. 80. Academic Press, New York.

Tebbens, B. D. (1968).—Gaseous pollutants in the air. In *"Air Pollution"*. A. C. Stern ed., Vol. 1, p. 41. Academic Press, New York.

Vines, R. G., Gibson, L., Hatch, A. B., King, N. K., MacArthur, D. A., Packham, D. R. and Taylor, R. J. (1971).—On the nature, properties and behaviour of bush-fire smoke. *C.S.I.R.O. Division of Applied Chemistry Technical Paper* 4: No. 1.

Whittaker, E. T. and Robinson, G. (1944).—*"The Calculus of Observations"*. 4th Ed. Blackie and Sons, London and Glasgow.

Zimmer, C. E. and Larsen, R. I. (1965).—Calculating air quality and its control. *J. Air Poll. Control Assn.* 15: 565.